

## DESCRIPTION

## Polycarbonate and Method for Production thereof.

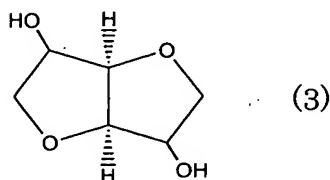
## 5 Technical Field

The present invention relates to polycarbonates containing a moiety which can be derived from a polysaccharide of renewable resources and having an excellent heat resistance, and methods for producing thereof.

## 10 Background Art

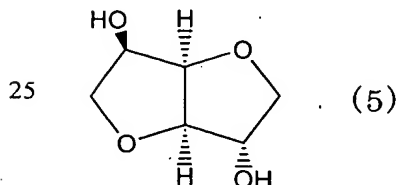
Polycarbonates are generally produced by using raw materials which can be obtained from oil resources. Because of the concern about the exhaustion of oil resources, it is desired to produce polycarbonates by using raw materials obtainable from renewable resources such as plants.

15 On the other hand, an ether diol expressed by the following formula (3) can be easily prepared from renewable resource, for example, polysaccharide, starch or the like.



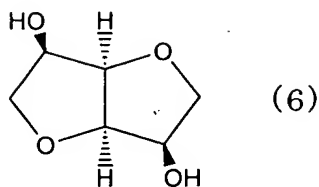
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The ether diol has three kinds of stereoisomers. In concrete terms, they are 1,4: 3,6-dianhydro-D-sorbitol (hereafter, this compound will be referred as to "isosorbide" in this description) expressed by the following formula (5),

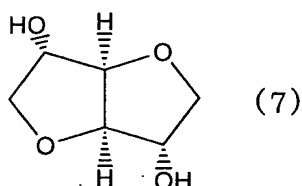


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1,4: 3,6-dianhydro-D-mannitol (hereafter, this compound will be referred as to "isomannide" in this description) expressed by the following formula (6),



and 1,4:3,6-dianhydro-L-iditol (hereafter, this compound will be referred as  
5 to "isoidide" in this description) expressed by the following formula (7).



Isosorbide, isomannide and isoidide can be produced from D-glucose,  
10 D-mannose and L-idose, respectively. For example, isosorbide can be produced by hydrogenating D-glucose followed by dehydration with an acid catalyst.

Heretofore, it was studied to incorporate especially isosorbide among the above-mentioned ether diols into a polycarbonate as the main  
15 monomer (for example, German unexamined patent publication No. 2938464, Journal fuer praktische Chemie, p. 298-310, vol. 334, 1992, Macromolecules, p. 8077-8082, vol. 29, 1996, and Journal of Applied Polymer Science, p. 872-880, vol. 86, 2002).

However, isosorbide-derived polycarbonates have a problem of poor  
20 moldability, which is caused by extremely high glass transition temperatures and melt viscosities due to their rigid structures.

Further, methods for producing copolycarbonates which contain isosorbide and a diphenol of various types were reported (for example, JP-A  
56-110723, Macromolecular Chemistry and Physics, p. 2197-2210, vol. 198,  
25 1997, Journal of Polymer Science: Part A, p. 1611-1619, vol. 35, 1997, and Journal of Polymer Science: Part A, p.1125-1133, vol. 37, 1999). These copolycarbonates have problems that the diphenols are derived from oil.

On the other hand, speaking of polycarbonates which are derived

from aliphatic diols, glass transition temperatures of the polycarbonates which are derived from ethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol or the like are 0-5°C, -35°C, -41°C and -50°C, respectively (for example, Journal of Polymer Science: Polymer Letters Edition, p.599-602, vol. 18, 1980, Macromolecular Chemistry and Physics, p.97-102, vol. 199, 1998, and Polycarbonate resin handbook, edited by Seiichi Honma, Nikkan Kogyo Shinbun Co. p. 21, 1992).

It is possible to use renewable resources as these aliphatic diols, but aliphatic diol-derived polycarbonates are usually oily substances or solids with low melting points at the room temperature due to their flexible structures, and they have shortcomings of poor heat resistances. Polycarbonate copolymers derived from an aliphatic diol and having a higher glass transition temperature have never been reported.

Further, although reports concerning copolycarbonates of isosorbide and an aliphatic diol are few, as one of them we can find a report of copolycarbonates of an aliphatic diol such as 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol or 1,10-decanediol, and isosorbide (for example, Okada et al, Abstract of the seventh open symposium on "Polymers with low environmental loads": Construction of a sustainable material system based on production of plastics with low environmental loads from renewable resources, Scientific Research on Priority Areas (B) supported by Grant-in-Aid for Scientific Research of Ministry of Education, Culture, Sports, Science and Technology, p. 26-29, 2002, and Journal of Polymer Science: Part A, p. 2312-2321, vol. 41, 2003).

These polycarbonates are block copolymers or random copolymers, and their glass transition temperatures become lower with increasing lengths of aliphatic chains. The temperatures have been determined as 65°C or 59°C, 26°C or 20°C, 12°C or 23°C, and -1°C or 7°C, respectively, and they are poor in heat resistances.

Further, JP-A 2003-292603, which was published after the date of the basic application of the present invention, describes a thermoplastic molding material containing a polycarbonate compound obtainable from isosorbide. Although the glass transition temperature of the thermoplastic molding material is sufficiently higher than the room temperature, further

improvement of heat resistance is desired.

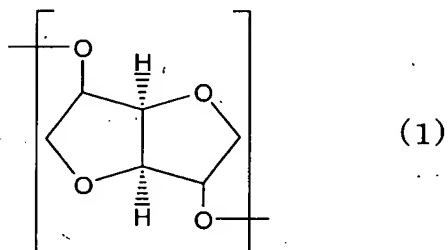
### Disclosure of the Invention

It is an object of the present invention to provide new polycarbonates  
5 containing a moiety which can be derived from renewable resources and  
having an excellent heat resistance and moldability.

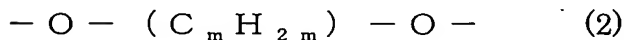
Another object of the present invention is to provide a process which  
is excellent in cost and through which the polycarbonates can be simply  
produced.

10 Further other objects and merits of the present invention will be  
made clear by the following explanations.

The present invention relates to polycarbonates containing an ether  
diol residue producible from a polysaccharide and expressed by the following  
formula (1),



and a diol residue expressed by the following formula (2)



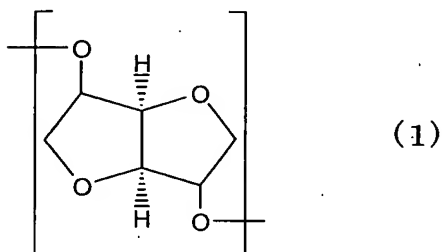
(here, m is an integer of 2 to 12), wherein said ether diol residue amounts to  
65-98 wt.% of all the diol residues, and having glass transition temperatures  
of 90°C or higher. The present invention also relates to a method for  
producing the polycarbonates.

### Best Mode for Carrying Out the Invention

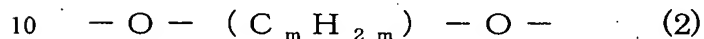
25 Hereafter, the mode for carrying out the present invention will be  
explained further in detail, while the examples and explanations mentioned  
below are for exemplifying the present invention, and the present invention

is not restricted by them. It is needless to say that other modes for carrying out the invention can be within the scope of the present invention as long as they conform to the objects of the present invention.

The polycarbonate of the present invention contains an ether diol residue expressed by the following formula (1)

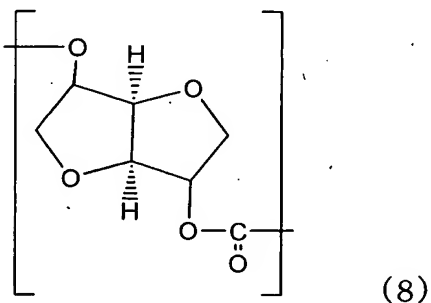


and a diol residue expressed by the following formula (2)

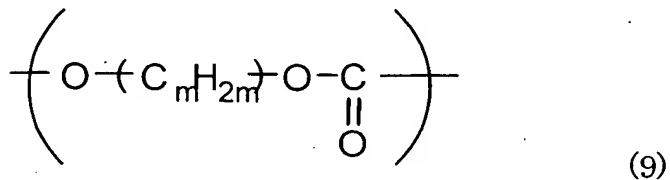


(here, m is an integer of 2-12), wherein the ether diol residue amounts to 65-98 wt.% of all the diol residues, and the polycarbonate has a glass transition temperature of 90°C or higher. It is preferable that the ether diol residues amount to 80-98 wt.% of all the diol residues.

That is, the polycarbonates of the present invention have a repeating unit moiety of formula (8)



and a repeating unit moiety of formula (9)



(here, m is an integer of 2 to 12).

When the content of the ether diol residue becomes lower than the above-mentioned range, the glass transition temperature of the resin to be obtained decreases, and the degree of polymerization hardly increases, so that the polymer becomes brittle. When the content of the ether diol exceeds the above-mentioned range, the glass transition temperature and the melt viscosity become extremely high, so that moldability becomes poor.

In the polycarbonate of the present invention, the diol residue expressed by the above-mentioned formula (2) is preferably at least one kind selected from the group consisting of an ethylene glycol residue, a 1,3-propanediol residue, a 1,4-butanediol residue, a 1,5-pentanediol residue and a 1,6-hexanediol residue.

It is also preferable that the polycarbonate contains another diol residues besides the ether diol residues and the diol residues expressed by the above-mentioned formula (2). Examples of another diol residues are alicyclic alkylenediols such as cyclohexanediol and cyclohexanedimethanol, aromatic diols such as dimethanolbenzene and diethanolbenzene, bisphenols etc. In this case, it is preferable that the total content of the third diol residues do not exceed 50 parts by weight against 100 parts by weight of the glycol residue of the above-mentioned formula (2).

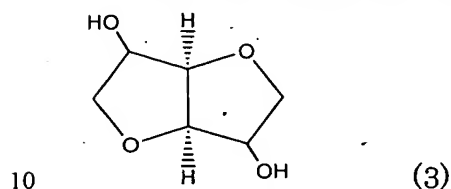
Further, it is preferable that at least two kinds or more of the diol residues expressed by the above-mentioned formula (2) are used. When two kinds or more of the diol residues expressed by the above-mentioned formula (2) are used, the ratio of the diol residues is not specially restricted. It is preferable to use combinations of two kinds or more of diols selected from an ethylene glycol residue, a 1,3-propanediol residue, a 1,4-butanediol residue, a 1,5-pentanediol residue and a 1,6-hexanediol residue which have specially high degradability in nature. A more preferable combination is, for example, a 1,6-hexanediol residue and a 1,3-propanediol residue, or a 1,6-hexanediol residue and a 1,4-butanediol residue.

The polycarbonates of the present invention have a glass transition temperature of 90°C or more. The glass transition temperature is an important factor for heat resistance of a molded product and melt moldability. The glass transition temperature is preferably not less than

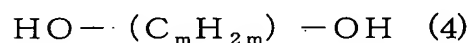
100 °C nor more than 160 °C for keeping practically sufficient heat resistance and moldability.

Further, the polycarbonates of the present invention have a reduced viscosity of preferably 0.1 dl/g or more, more preferably 0.35 dl/g or more, and further more preferably 0.6 dl/g or more. When the reduced viscosity is in this range, the polycarbonates have good melt fluidity, and further they have sufficient mechanical strength.

The polycarbonates of the present invention can be produced from an ether diol expressed by the following formula (3),



a diol expressed by the following formula (4),



(here, m is an integer of 2 to 12)

and a carbonic acid diester by a melt polymerization method.

15 Concrete examples of the ether diol include isosorbide, isomannide and isoidide, which are expressed by the above-mentioned formulae (5), (6) and (7), respectively, and others.

20 These polysaccharide-derived ether diols are materials which can be obtained also from biomass, and one of the materials which are called renewable resources. Isosorbide can be produced by hydrogenating D-glucose, which is obtainable from starch, and dehydrating the hydrogenated product. The other ether diols can be produced by the similar reactions using different starting materials.

Especially, a polycarbonate containing the isosorbide residue as the ether diol residue is preferable. Isosorbide is an ether diol which can easily be produced from starch or the like, so that it is abundantly obtainable as a raw material, and in addition, it is superior to isomannide and isoidide in all the points of easiness in production, excellences of properties and broad ranges of usage.

30 When the polycarbonate of the present invention contains the isosorbide residue as the ether diol residue, it is preferable that the

isosorbide residue amounts to 65-98 wt.% of all the diol residues. It is more preferable that it amounts to 80-98 wt.% of all the diol residues.

The carbonic acid diester which is used in the production of the polycarbonate of the present invention is, for example, diphenyl carbonate, dinaphthyl carbonate, bis(diphenyl)carbonate, dimethyl carbonate, diethyl carbonate, dibutyl carbonate or the like. Among these carbonic acid diesters, diphenyl carbonate is preferable from the points of view of reactivity and cost.

In the production method of the present invention, a diol and a carbonic acid diester, which are raw materials, are subjected to a preliminary reaction by heating them at atmospheric pressure preferably in the presence of a polymerization catalyst, and subsequently they are stirred under reduced pressure while they are heated at 280°C or less to distil away the formed phenol. The reaction system is preferably kept in an atmosphere of a gas such as nitrogen which is inert against the raw materials, the reaction mixture and the reaction product. Besides nitrogen, the other inert gas such as argon is available.

At the initial stage of the reaction, it is preferable to carry out the heating reaction at atmospheric pressure. This progresses an oligomer forming reaction, so that when an aromatic alcohol such as phenol or an aliphatic alcohol is distilled away by reducing pressure at the later stage of the reaction, it is prevented that unreacted monomer distills away to break the mole balance and lower the degree of polymerization. In the production method of the present invention, the reaction can be promoted by properly removing the aromatic alcohol or aliphatic alcohol from the system (reactor). For this purpose, it is effective and preferable to reduce the pressure of the system.

In the production method of the present invention, it is preferable to suppress the reaction temperature as low as possible in order to prevent the decomposition of the ether diol, and obtain a resin less colored and having a high viscosity. However, for promoting the polymerization reaction properly, the polymerization temperature is preferably in the range from 180°C to 280°C, more preferably in the range from 230°C to 260°C.

In the production method of the present invention, it is preferable to



use catalysts. Usable catalysts are (i) a nitrogen-containing basic compound, (ii) an alkali metal compound, (iii) an alkaline earth metal compound etc. These can be used singly or in combination of two kinds or more, and combined usages of (i) and (ii), (i) and (iii), and (i), (ii) and (iii) are  
5 often preferable.

A preferable example of (i) is tetramethylammonium hydroxide, and preferable examples of (ii) are sodium salts, and among them the usage of 2,2-bis(4-hydroxyphenyl)propane disodium salt is especially preferable.

Further, to the polycarbonates of the present invention, various  
10 function-imparting agents are optionally added according to the use of the polycarbonates. Such agents are, for example, heat stabilizers, stabilization adjuvants, plasticizers, antioxidants, photostabilizers, nucleating agents, heavy metal-inactivating agents, flame retardants, lubricants, antistatic agents, ultraviolet absorbers etc.

Further, depending on the use, the polycarbonates of the present  
15 invention are optionally compounded with various organic or inorganic fillers, fibers etc. The examples of the filler are carbon, talc, montmorillonite, hydrotalcite etc., and the examples of the fiber are various synthetic fibers, glass fibers, quartz fibers, carbon fibers etc. in addition to  
20 natural fibers such as kenaf.

As mentioned above, we can obtain polycarbonates containing a moiety which can be derived from renewable resources, and having excellent heat resistance.

By virtue of excellent heat resistance, the polycarbonates of the  
25 present invention can be widely used for various uses including optical parts such as optical sheets, optical disks, information disks, and optical lenses and prisms, various machine parts, building materials, car components, and various resin trays and dishes. The polycarbonates can be used especially preferably as film molded items such as optical sheets among these uses.

By virtue of biodegradability, the polycarbonates of the present  
30 invention can be used as films and sheets for agricultural materials including green house films, mulch films etc., packaging films and sheets for uses including food wrapping, general packaging, compost bags etc., industrial materials including tapes etc., various packaging containers etc.

and molded articles for various uses in which the prevention of environmental contamination are needed.

Further, the polycarbonates of the present invention can be used after they are mixed and alloyed with a bio-based polymer, a synthetic resin, a rubber or the like of various types, for example, an aromatic polyester, an aromatic polycarbonate, a polyamide, polystyrene, a polyolefin, polyacrylic acid, ABS, a polyurethane etc. in addition to polylactic acid and an aliphatic polyester.

## 10 Examples

Hereafter, the present invention will be explained in detail with examples, while the present invention is not restricted by the examples.

Evaluations in the examples were carried out as follows. Physical properties are shown collectively in Table 1.

15 (1) Measurement of glass transition temperature: Glass transition temperatures ( $T_g$ ) were measured in a nitrogen stream at a temperature elevation rate of  $20^{\circ}\text{C}/\text{min}$  by using a differential scanning calorimeter of 910 Model manufactured by DuPont Co.

(2) Measurement of reduced viscosity: Reduced viscosities ( $\text{dl/g}$ ) were measured on a solution obtained by dissolving 120 mg of a polycarbonate sample in 10 ml of a mixed solvent of phenol/tetrachloroethane (volume ratio of 50/50) at  $30^{\circ}\text{C}$  using an Ubbelohde viscometer.

(3) Evaluation of moldability: Moldabilities were determined by molding a polycarbonate sample at a projection temperature of  $240^{\circ}\text{C}$  and a mold temperature of  $80^{\circ}\text{C}$  using a small-sized injection molding machine manufactured by Nissei Plastic Industrial Co., Ltd.. Tensile tests were carried out according to ASTM D-683, and bending tests were carried out according to ASTM D-790.

30 (4) Evaluation of biodegradability: Into 200 g of a commercially available leaf mold (a bark compost manufactured by Sanyo-Bark) was added 1 liter of reservoir water, the mixture was aerated for 30 minutes or more at about  $30^{\circ}\text{C}$  in a hot water bath. Then, the mixture was filtered through a filter paper. Into the filtrate was added 100 ml of optimized

testing culture solution A (a solution obtained by dissolving 37.5 g of potassium dihydrogenphosphate, 72.9 g of disodium hydrogenphosphate and 2.0 g of ammonium chloride in 1 liter of ion exchanged water), and the total volume of the mixture was made 2 liters. The obtained solution was charged into a container that was placed in a constant temperature bath at 50°C, which is close to the compost condition, and it was aerated at a ventilation volume of 200 ml/min with pressurized air. The half of the culture solution was replaced with a newly prepared solution media every fourth or fifth day.

10        A test piece weighing about 200 mg was cut out from a film approximately 20  $\mu$  m in thickness obtained by casting a solution prepared by dissolving a test polymer in dichloromethane on a glass base. The test piece was charged into a commercially available nonwoven cloth bag, and the bag was placed in the above-mentioned container. The bag was taken  
15        out after 3 months. The weight decreasing rate of the test piece was determined, and thus the biodegradability was evaluated.

#### Example 1

      Into a reactor were charged 29.23 parts by weight of isosorbide, 1.51  
20        parts by weight of ethylene glycol and 49.48 parts by weight of diphenyl carbonate, and further  $2 \times 10^{-3}$  parts by weight of tetramethylammonium hydroxide ( $1 \times 10^{-4}$  mol of this compound to 1 mol of the diol component) and  $30 \times 10^{-4}$  parts by weight of 2,2-bis(4-hydroxyphenyl)propane disodium salt ( $0.5 \times 10^{-6}$  mol of this compound to 1 mol of the diol component), and they  
25        were melted at 180°C under a nitrogen atmosphere.

      The reaction was carried out for 20 minutes under stirring while the formed phenol was distilled away by reducing the inside pressure of the reactor to  $13.3 \times 10^{-3}$  MPa. Subsequently, after the temperature was raised to 200°C, the pressure was reduced gradually, and the reaction was carried  
30        out for 25 minutes at  $4.00 \times 10^{-3}$  MPa while phenol was distilled away. Further, the reaction was carried out for 10 minutes after the temperature was raised to 215°C.

      Subsequently, the pressure was gradually reduced, the reaction was carried out for 10 minutes at  $2.67 \times 10^{-3}$  MPa, and for 10 minutes at  $1.33 \times 10^{-3}$

MPa. When the pressure reached to  $4.00 \times 10^{-5}$  MPa, the temperature was gradually raised up to  $250^{\circ}\text{C}$ , and finally the reaction was carried out further for 1 hour at  $250^{\circ}\text{C}$  at  $6.66 \times 10^{-5}$  MPa.

The obtained polymer had a reduced viscosity of 0.353 dl/g and a glass transition temperature of  $157.4^{\circ}\text{C}$ .

#### Examples 2 to 5

Isosorbide, ethylene glycol and diphenyl carbonate having amounts shown in Table 1 were charged into a reactor. As polymerization catalysts, tetramethylammonium hydroxide and 2,2-bis(4-hydroxyphenyl)propane disodium salt were charged at the same ratios of concentrations as Example 1, they were melted at  $180^{\circ}\text{C}$  under a nitrogen atmosphere, and polymerization reaction was carried out in the same manner as Example 1 to obtain a polymer. The reduced viscosity and glass transition temperature of the polymer are shown in Table 1.

#### Example 6 to 8

Isosorbide, 1,3-propanediol and diphenyl carbonate having amounts shown in Table 1 were charged into a reactor. As polymerization catalysts, tetramethylammonium hydroxide and 2,2-bis(4-hydroxyphenyl)propane disodium salt were charged at the same ratios of concentrations as Example 1, and they were melted at  $180^{\circ}\text{C}$  under a nitrogen atmosphere.

Polymerization reaction was carried out in the same manner as Example 1 to obtain a polymer. The reduced viscosity and glass transition temperature of the polymer are shown in Table 1.

By using the polymer obtained in Example 6, a dumbbell-shaped molded piece, that is, a tabular molded piece of 120 mm x 12 mm x 3 mm was produced, and the moldability was evaluated. The results are shown in Table 3.

A film was produced from the polymer obtained in Example 6, and the biodegradability was evaluated. The reduction in weight of the test piece was 15.9%.

#### Examples 9 to 10

Isosorbide, 1,4-butanediol and diphenyl carbonate having amounts shown in Table 1 were charged into a reactor. As polymerization catalysts, tetramethylammonium hydroxide and 2,2-bis(4-hydroxyphenyl)propane disodium salt were charged at the same ratios of concentrations as Example 1, and they were melted at 180 °C under a nitrogen atmosphere. Polymerization reaction was carried out in the same manner as Example 1 to obtain a polymer. The reduced viscosity and glass transition temperature of the polymer are shown in Table 1.

By using the polymer obtained in Example 10, a dumbbell-shaped molded piece, that is, a tabular molded piece of 120 mm x 12 mm x 3 mm was produced, and the moldability was evaluated. The results are shown in Table 3.

#### Examples 11 to 12

Isosorbide, 1,5-pentanediol and diphenyl carbonate having amounts shown in Table 1 were charged into a reactor. As polymerization catalysts, tetramethylammonium hydroxide and 2,2-bis(4-hydroxyphenyl)propane disodium salt were charged at the same ratios of concentrations as Example 1, and they were melted at 180 °C under a nitrogen atmosphere. Polymerization reaction was carried out in the same manner as Example 1 to obtain a polymer. The reduced viscosity and glass transition temperature of the polymer are shown in Table 1.

#### Examples 13 to 16

Isosorbide, 1,6-hexanediol and diphenyl carbonate having amounts shown in Table 2 were charged into a reactor. As polymerization catalysts, tetramethylammonium hydroxide and 2,2-bis(4-hydroxyphenyl)propane disodium salt were charged at the same ratios of concentrations as Example 1, and they were melted at 180 °C under a nitrogen atmosphere. Polymerization reaction was carried out in the same manner as Example 1 to obtain a polymer. The reduced viscosity and glass transition temperature of the polymer are shown in Table 2.

By using the polymer obtained in Example 15, a dumbbell-shaped molded piece, that is, a tabular molded piece of 120 mm x 12 mm x 3 mm

was produced, and the moldability was evaluated. The results are shown in Table 3.

A film was produced from the polymer obtained in Example 11, and the biodegradability was evaluated. The reduction in weight of the test  
5 piece was 15.6%.

#### Example 17 to 21

Isosorbide, 1,6-hexanediol, 1,3-propanediol and diphenyl carbonate having amounts shown in Table 2 were charged into a reactor. As  
10 polymerization catalysts, tetramethylammonium hydroxide and 2,2-bis(4-hydroxyphenyl)propane disodium salt were charged at the same ratios of concentrations as Example 1, and they were melted at 180°C under a nitrogen atmosphere. Polymerization reaction was carried out in the same manner as Example 1 to obtain a polymer. The reduced viscosity  
15 and glass transition temperature of the polymer are shown in Table 2.

By using the polymer obtained in Example 17, a dumbbell-shaped molded piece, that is, a tabular molded piece of 120 mm x 12 mm x 3 mm was produced, and the moldability was evaluated. The results are shown  
20 in Table 3.

#### Example 22

Into a reactor were charged 23.38 parts by weight of isosorbide, 2.36 parts by weight of 1,6-hexanediol, 1.80 parts by weight of 1,4-butanediol and 42.84 parts by weight of diphenyl carbonate. As polymerization catalysts,  
25 tetramethylammonium hydroxide and 2,2-bis(4-hydroxyphenyl)propane disodium salt were charged at the same ratios of concentrations as Example 1, and they were melted at 180 °C under a nitrogen atmosphere.

Polymerization reaction was carried out in the same manner as Example 1 to obtain a polymer. The reduced viscosity and glass transition  
30 temperature of the polymer are shown in Table 2.

#### Example 23

Into a reactor were charged 24.84 parts by weight of isosorbide, 1.80 parts by weight of 1,4-butanediol, 1.24 parts by weight of ethylene glycol

and 44.99 parts by weight of diphenyl carbonate. As polymerization catalysts, tetramethylammonium hydroxide and 2,2-bis(4-hydroxyphenyl)propane disodium salt were charged at the same ratios of concentrations as Example 1, and they were melted at 180°C under a nitrogen atmosphere. Polymerization reaction was carried out in the same manner as Example 1 to obtain a polymer. The reduced viscosity and glass transition temperature of the polymer are shown in Table 2.

#### Comparative Examples 1 to 4

Isosorbide shown in Table 2 and various types of diphenyl carbonate 44.1 parts by weight were charged into a reactor. As polymerization catalysts, tetramethylammonium hydroxide and 2,2-bis(4-hydroxyphenyl)propane disodium salt were charged at the same ratios of concentrations as Example 1, and they were melted at 180°C under a nitrogen atmosphere.

Polymerization reaction was carried out in the same manner as Example 1 to obtain a polymer. The reduced viscosity and glass transition temperature of the polymer are shown in Table 2.

Table 3

	Example 6	Example 10	Example 15	Example 17
Tensile modulus [MPa]	3100	2632	2426	2534
Tensile stress at yield [MPa]	85	74.2	63	70.4
Elongation at break[%]	4.6	5.5	4.8	5.3
Elongation at yield [%]	15	—	4.8	—
Flexural modulus [MPa]	2993	3327	3066	2742
Flexural strength [MPa]	37	143	128	118